Effect of Mineral Reactions on the Hydraulic Properties of Unsaturated Soils: Model Development and Application

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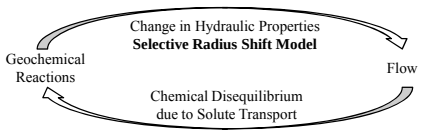
ABSTRACT

We present the development of a new model for feedback of geochemical reactions on flow in porous media through alteration of hydraulic properties and its integration into a simulator for unsaturated flow and solute transport with comprehensive geochemical reactions. Precipitation/dissolution reactions induce changes in the pore radii of water-filled pores, and, consequently, affects flow in porous media. The *selective radius shift* model was developed to relate changes in mineral volume due to precipitation/dissolution to changes in hydraulic properties of unsaturated soils. The model considers the dependency of the amount of mineral precipitation/dissolution within a pore on the local pore volume. Furthermore, it accounts for precipitation/dissolution taking place only in the water-filled part of the pore space. The pore bundle concept was used to relate the pore-scale process of dissolution/precipitation to changes in macroscopic soil hydraulic properties. In the numerical model, the change in mineral volume at a discrete time step leads to a discontinuous pore-size distribution, because only the water-filled pores are affected. This pore-size distribution is converted back to a discontinuous soil moisture characteristic to which, at every time step, a new water retention curve is fitted under physically plausible constraints. The model equations were derived for the commonly used van Genuchten/Mualem hydraulic properties. Together with the selective radius shift model, a head-based solution of Richards' equation for aqueous phase flow was implemented into the geochemical modelling framework PHREEQC, thereby making available PHREEQC's comprehensive geochemical reactions. The model was applied to kinetic halite dissolution and calcite precipitation as a consequence of cation exchange in a variety of unsaturated flow situations. These applications show marked changes in the soil's hydraulic properties due to mineral precipitation/dissolution and the dependency of these changes on the water content.



I. SELECTIVE RADIUS SHIFT MODEL (within the framework of a numerical model for unsaturated flow and geochemical reactions)

- The initial pore-size distribution of a soil is derived from its soil moisture characteristic curve using the pore bundle concept (Young-Laplace equation).
- Pore radii of the water-filled part of the pore-size distribution are modified by dissolution/precipitation such that
  - i. the volume change of the pore space is equal to the change in mineral volume calculated by the geochemical reaction model; and
  - ii. the volume change of individual pore sizes is proportional to the actual pore volume.
- The resulting discontinuous pore-size distribution is converted back to a discontinuous soil moisture characteristic curve.
- A single continuous water retention function is fitted to the discontinuous characteristics that results from pore-size selective mineral reactions.

This procedure is applied to each cell in the model domain and at every time step, if mineral reactions occur.

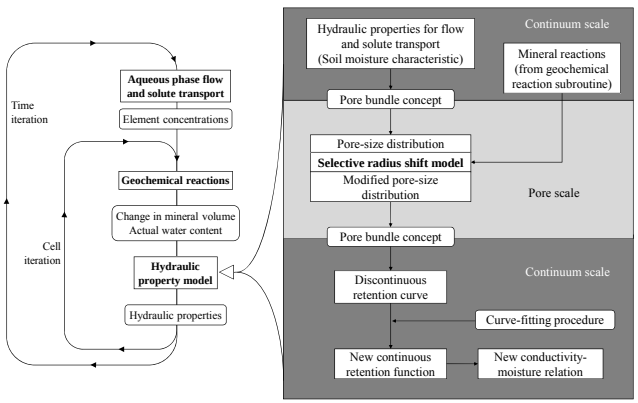


Fig. 1: Program flow and structure of hydraulic property calculations with the selective radius shift model.

II. IMPLEMENTATION OF UNSATURATED AQUEOUS PHASE FLOW INTO PHREEQC

- Fully implicit, central finite difference scheme for liquid phase flow according to head-based Richards' equation, directly implemented into PHREEQC without coupling to other software
- Flow results from the solute transport equation applied to every element in the element assembly of the liquid phase ⇒ eliminates conceptual difference between solute and solvent
- Direct accessibility of PHREEQC's databases and comprehensive geochemical reactions

Model capabilities:

– Unsaturated transient flow in heterogeneous porous media
together with:
– Solution speciation
– Irreversible reactions
– Mineral phase reactions (including solid solutions)
– Gas phase reactions
– Redox reactions
– Cation exchange
– Surface adsorption on variable charge adsorption sites (including diffuse layer)
– Kinetic reactions

Extensive code verification was carried out using analytical solutions and HYDRUS-1D. Fig. 2 shows the excellent agreement with HYDRUS-1D for initial and boundary conditions:

$t = 0$ min, $z \leq 25$ cm, $h = -1000$ cm,
$t \geq 0$ min, $z = 0$ cm, $h = -1000$ cm,
$t \geq 0$ min, $z = 25$ cm, $h = 0$ cm.

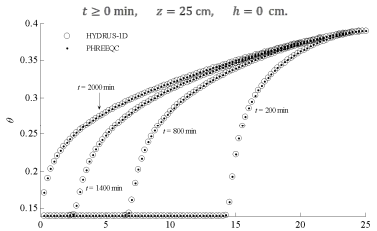


Fig. 2: Verification for upward diffusion in homogenous sandy clay loam at subsequent times. θ: volumetric water content, z: distance downwards from the soil surface.

III. KINETIC HALITE DISSOLUTION

Simulation properties:

- Infiltration into loamy sand (column length: 50 cm, cross section: 10cm²), amended with 150 mol (8.77 kg) of halite
- Kinetic dissolution of halite phase according to

$$\frac{d\eta_{Na,Cl}}{dt} = k\,(1-\Omega)$$

k: rate constant (molM^{-1}T^{-1}) takes as 0.2 mol L^{-1} min^{-1}
$\eta_{Na,Cl}$: molar concentration of Na and Cl
Ω: saturation ration

- Hydraulic property model: **van Genuchten/Mualem**

Steady state flow

- Changes in pore-size distribution and soil moisture characteristics dependent on water saturation. Dissolution occurs up to the capillary radius that corresponds to the moisture content. At low soil moisture contents, changes in mineral volumes only affect small pore sizes. At high soil moisture contents the entire pore spectrum is affected.
- The change in pore volume is proportional to the pore volume. Thus larger pores undergo large changes in pore radii r than smaller pores.
- However, depending on the pore-site distribution, large pores contribute usually less to the total pore volume.

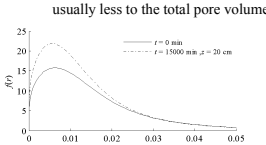


Fig. 3: Development of pore-size distribution due to kinetic halite dissolution at reduced moisture content $\Theta \approx 0.41$.

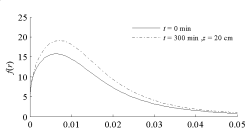


Fig. 4: Development of pore-size distribution due to kinetic halite dissolution at reduced moisture content $\Theta \approx 1$.

Transient infiltration

- Dissolution/precipitation in transient moisture conditions (a) results in heterogeneous hydraulic properties.
- Changes in saturated water content (b) represent changes in mineral volume.
- Changes in the van Genuchten-parameter n (d) indicate changes in the shape of the pore size distribution and water retention function. These shape-changes are larger when dissolution/precipitation proceeds at lower soil moisture (at column inflow).
- Saturated conductivity (e) increases less in places where dissolution proceeds at lower soil moisture content ⇒ Changes of the largest pore sizes has a bigger influence on conductivity, than the same volume change in small pores.

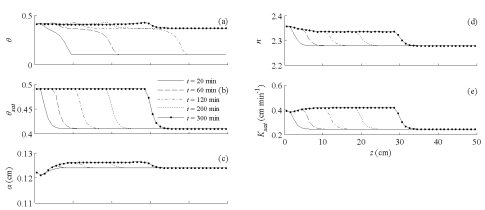


Fig. 5: Change in parameters of the van Genuchten/Mualem model due to kinetic halite dissolution during transient infiltration.(a) moisture content, (b) saturated moisture content, (c) scaling parameter α, (d) shape parameter n, (e) saturated hydraulic conductivity.

IV. CALCITE PRECIPIATION DUE TO CATIO EXCHANGE

The example is motivated by the frequently observed permeability reduction in reactive barriers, where minerals precipitate due to adsorption-desorption processes .

Simulation properties:

- Infiltration into clay loam (column length: 20 cm, cation exchanger [$z \geq 10$ cm]: 4 eq/kg soil)
- Initial exchanger saturated with calcium, inflowing solution at solubility limit of natron, equilibration with calcite within the column.
- Hydraulic property model: **van Genuchten/Mualem**

Results:

- Arrival of sodium front [Fig. 6(a)] at exchanger ($z \geq 10$ cm) leads to exchange of calcium by sodium [Fig. 6(b-d)] and triggers precipitation of calcite [Fig. 6(e)] in the water-filled pore spectrum.
- Precipitation leads to a reduction in saturated water content [Fig. 7(b)] and a general reduction in saturated hydraulic conductivity [Fig. 7(e)] . At same water contents, hydraulic conductivity rises because flow is subsequently carried through larger pores (not shown).
- Increasing the n-parameter [Fig. 7(d)] indicates a shift of the pore-size distribution towards larger pores as a result of precipitation in small pores. Thus, n increases most where precipitation occurs at low water contents (top boundary of the reactive barrier).

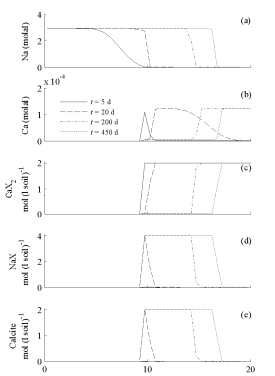


Fig. 6: Cation exchange process in high capacity exchanger at $z \geq 10$ cm followed by calcite precipitation.

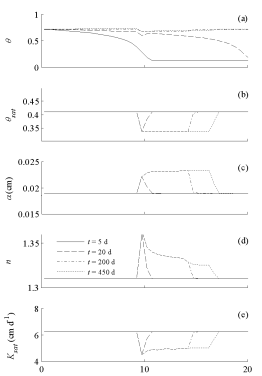


Fig. 7: Evolution of hydraulic properties due calcite precipitation.

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